

BIO-COMPOSITE MATERIALS AS ALTERNATIVES TO PETROLEUM-BASED COMPOSITES FOR AUTOMOTIVE APPLICATIONS

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Abstract

Natural/Bio-fiber composites (Bio-Composites) are emerging as a viable alternative to glass fiber reinforced composites especially in automotive applications. Natural fibers, which traditionally were used, as fillers for thermosets, are now becoming one of the fastest growing performance additives for thermoplastics. Advantages of natural fibers over man-made glass fiber are: low cost, low density, competitive specific mechanical properties, reduced energy consumption, carbon dioxide sequestration, and biodegradability. Natural fibers offer a possibility to developing countries to use their own natural resources in their composite processing industries.

The combination of bio-fibers like Kenaf, Hemp, Flax, Jute, Henequen, Pineapple leaf fiber and Sisal with polymer matrices from both non-renewable and renewable resources to produce composite materials that are competitive with synthetic composites requires special attention i.e. biofiber-matrix interface and novel processing. Natural fiber reinforced polypropylene (PP) composites have attained commercial attraction in automotive industries. Needle punching techniques as well as extrusion followed by injection molding for natural fiber – PP composites as presently adopted in the industry need a “greener” technology - - powder impregnation technology.

Natural fiber – PP or natural fiber – polyester composites are not sufficiently eco-friendly due to the petro-based source as well as non-biodegradable nature of the polymer matrix. Sustainability, industrial ecology, eco-efficiency and green chemistry are forcing the automotive industry to seek alternative, more Eco-friendly materials for automotive interior applications. Using natural fibers with polymers (plastics) based on renewable resources will allow many environmental issues to be solved. By embedding bio-fibers with renewable resource based bio-polymers such as cellulosic plastic, corn-based plastic, starch plastic and soy-based plastic are continuously being developed at Michigan State University.

Background

A car made from grass may not sound sturdy, but

plant-based cars are the wave of the future. Researchers in our center at Michigan State University are working on developing materials from plants like Hemp, Kenaf, Corn straw and Grass to replace plastic and metal-based car



Figure1: Car Interiors from Natural Fiber – Polypropylene Composites

components. Automakers now see strong promise in natural fiber composites (1). Natural fiber like Hemp has higher strength to weight ratio than steel and is also considerably cheaper to produce. Natural fiber composites are emerging as a realistic alternative to glass-reinforced composites. While they can deliver the same performance for lower weight, they can also be 25-30 percent stronger for the same weight. Moreover, they exhibit a favorable non-brittle fracture on impact, which is another important requirement in the passenger compartment.

In the United States, 10 million to 11 million vehicles putter out each year and reach the end of their useful lives. A network of salvage and shredder facilities process about 96 percent of these old cars, about 25 percent of the vehicles by weight, including plastics, fibers, foams, glass and rubber, remains as waste. A car made mostly of heated, treated and molded bio-fiber would simply be buried at its lifetime, which would be consumed naturally by bacteria.

Interior parts from natural fiber – PP (Fig. 1- ref.2) and exterior parts from natural fiber – polyester



Figure 2: Exterior engine components from Natural Fiber – Polyester Composites

resins (Fig.2 – ref.2) are already in use (2). Ford has a long history of R&D on new materials (3). Figure 3 shows Hennery Ford performing a durability test with a fire axe on prototype car made of plastics derived from soybeans.



Figure 3: Soy protein plastic based composites (Henry Ford 1941)

Hennery Ford began experimenting with composites around 1940, initially using compressed soybeans to produce composite plastic-like components. During that period the petroleum-based chemicals were very cheap and so soy-based plastic could not find economical importance. After

a long decade with new environmental regulations and depletion and uncertainty of petroleum sources have

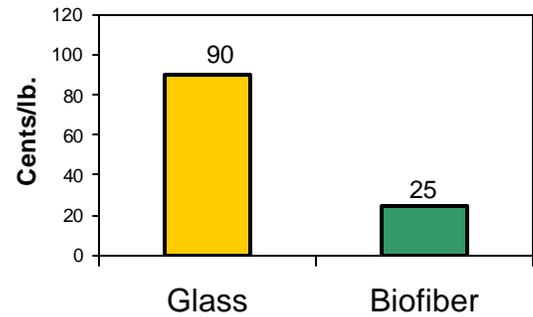


Figure 4: Cost comparison – E-glass vs. Bio-fiber

revived the interest of scientist to derive new generation of composite materials from soybean-based plastics. Researchers at our center in Michigan State University are

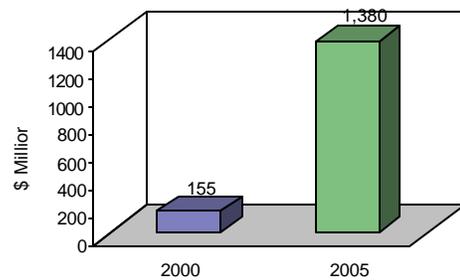


Figure 5: Projected growth of Natural Fiber Composites in North America

developing soy-based plastics for automotive and other infrastructure applications. Johnson Controls, Inc; has

Table 1: Weight savings: 21st Century Auto-parts

Light weight material	Material replaced	Mass reduction (%)	Relative cost (per part)
High strength steel	Mild steel	10	1
Aluminum	Steel, cast iron	40-60	1.3-2
Magnesium	Steel or cast iron	60-75	1,5-2.5
Magnesium	Aluminum	25-35	1-1.5
Glass fiber composites	Steel	25-35	1-1.5

started production (4) of door-trim panels from natural fiber and PP. The main motivation of using natural/bio-

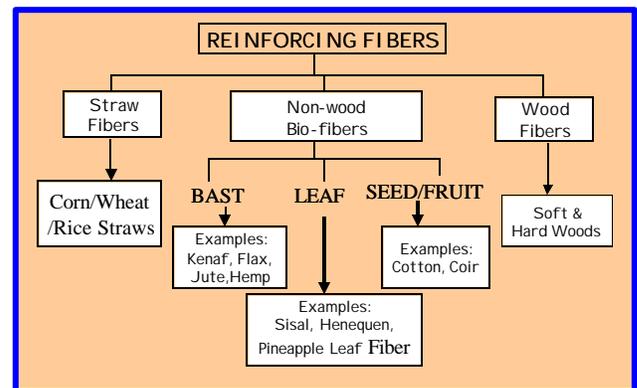
fibers like Kenaf and Hemp to replace glass fibers is the low cost (Fig.4), low density (~ 1/2 of glass), acceptable specific strength properties, enhanced energy recovery, CO₂ sequestration, and biodegradability. Auto companies are seeking materials with sound abatement capability as well as reduced weight for fuel efficiency. It is estimated that ~75% of a vehicle's energy consumption is directly related to factors associated with vehicle's weight, and it identifies as critical the need to produce safe and cost-effective light-weight vehicles. Natural fibers possess excellent sound absorbing efficiency and more shatter resistant and have better energy management characteristics than glass fiber based composites. In automotive parts, compared to glass composites, the composites made from natural fibers reduce the mass of the component; lowers the energy needed for production by 80% (5). It takes 6,500 BTUs of energy to produce one pound of Kenaf while it takes almost 4 times that much of energy (~23,500 BTUs) to produce one pound of glass fiber. To reduce vehicle weight; a shift away from steel alloys towards aluminum, plastics and composites has predicted that in near future polymer and polymer composites will comprise ~15% of a car weight (6). Table 1 (3) demonstrates how auto-parts save mass by going from steel to glass fiber reinforced plastic (GFRP). Our research has demonstrated that natural fiber composites

fiber composites (7). In the year 2000, the North American market for natural fiber composites exceeded \$150 million and by 2005, however this market is expected to reach nearly \$1.4 billion in sales due to a projected growth rate of 54% a year as demonstrated in Fig. 5.

Bio-Composites

A broad classification of natural fiber composites

Table 3: Classification of Bio-fibers

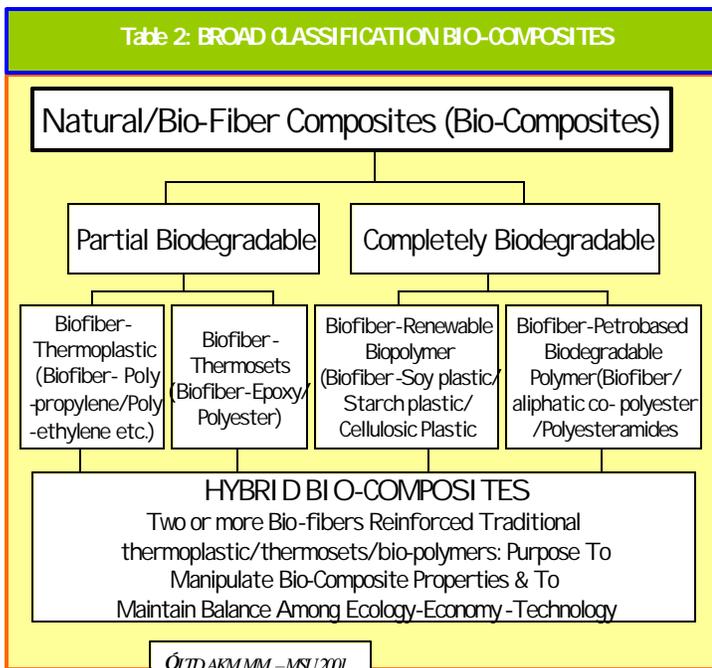


(Bio-Composites) is represented in Table 2. Bio-fiber being biodegradable and traditional thermoplastics (like polypropylene)/thermosets (like unsaturated polyester) being non-biodegradable; the bio-composites from such fiber reinforced polymer come under "Partial biodegradable" type. If the matrix resin/polymer is biodegradable, the bio-fiber reinforced bio-polymer composites would come under "Completely biodegradable" type. Two or more bio-fibers in combination on reinforcement with polymer matrix results "hybrid" bio-composites. The purpose of hybrid composites is the manipulation of properties of the resulting bio-composites. Bio-composite consists of reinforcing bio-fibers and matrix polymer system.

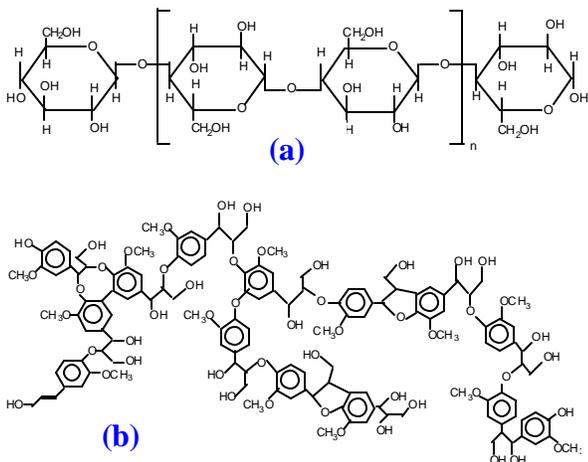
Reinforcing Bio-fiber

In fiber-reinforced composites, the fibers serve as reinforcements by giving strength and stiffness to the composite structure. Bio-fibers may be classified (Table 3) in to three broad categories: Straw fibers, Non-wood fibers and Wood fibers. So far as automotive applications are concerned; at the present level of technology, non-wood fibers like Hemp, Kenaf, Flax, and Sisal have attained commercial success in designing bio-composites from polypropylene. Another type of fiber i.e. grass fibers is gaining attention of scientists as a reinforcing fiber for automotive applications. All the natural reinforcing fibers are lingo-cellulosic in nature the principal component being cellulose and lignin (Scheme 1). The contents of cellulose and lignin vary from each bio-fiber to another.

Table 2: BROAD CLASSIFICATION BIO-COMPOSITES



show comparable or even superior mechanical properties over GFRP. Replacing glass by natural fiber would reduce the mass significantly. American market studies clearly identify the potential impact and opportunities for natural



Scheme 1: Structures of (a) Cellulose and (b) Lignin

Depending on their origin, non-wood natural fibers may be grouped in to: Bast: Kenaf, Flax, Jute, and Hemp; Leaf: Sisal, Henequen, and Pineapple leaf fiber; Seed: Cotton; Fruit: Coconut fiber or Coir. The tensile strengths of non-wood natural fibers are inferior to E-glass fiber. The density of glass being much higher than natural fibers; the specific strength of natural fibers are quite comparable to glass fiber. E-modulus and specific modulus (8) of natural fibers are comparable or even superior over E-glass fibers (Table 4).

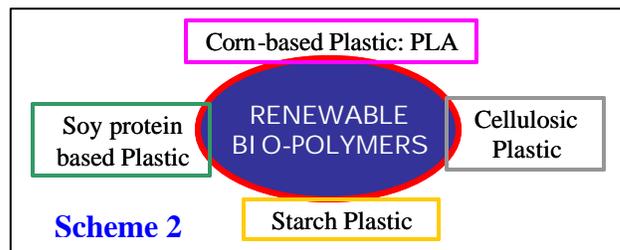
Table 4: Modulus comparison of glass and some important natural fibers (ref. 8 and partially corrected)

Fiber Type	Density (g/cm ³)	E-modulus (GPa)	Specific modulus (modulus/density)
E-glass	2.55	73	29
Hemp	1.48	70	47
Flax	1.4	60-80	43-57
Jute	1.46	10-30	7-21
Sisal	1.33	38	29
Coir	1.25	6	5
Cotton	1.51	12	8

Matrix Polymers

Among all the matrix polymers; polypropylene (PP) has attained much commercial success in bio-composites for automotive applications. Although unsaturated polyester resin can be used in bio-composite applications commercially, the non-recyclable nature of this thermoset resin over thermoplastic recyclable PP is hindering its growing importance. Bio-composites derived from natural fibers and traditional thermoplastics or thermosets are not fully environmentally friendly because

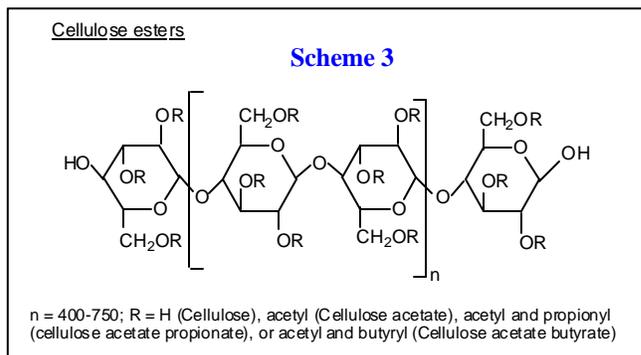
the matrix resins are petro-based and also non-biodegradable. However these bio-composites now



maintain a balance among ecology, economy and technology allowing them to be considered for applications in automotives.

Biopolymers derived from renewable resources (Scheme 2) are attracting the attention of scientists to replace traditional petro-based plastics in designing more eco-friendly bio-composites. Polylactic acid (PLA) is a highly versatile biodegradable polymer and is recently highlighted because it is derived from renewable resource like corn (9). The use of such PLA as a cost-effective alternative to commodity petro-based plastic will increase the demand for agricultural products. It comes under aliphatic polyester type of polymer and is a polymer of α -hydroxy acid.

Creating biodegradable products from waste materials is one way to make products environmentally friendly. Another way is to make products from sustainable resources. Cellulose from trees and cotton plants is taken as a substitute for petroleum feedstocks to make cellulosic plastic (10). One should take natural polymer – cellulose and then should react it to make derivitized biopolymer.



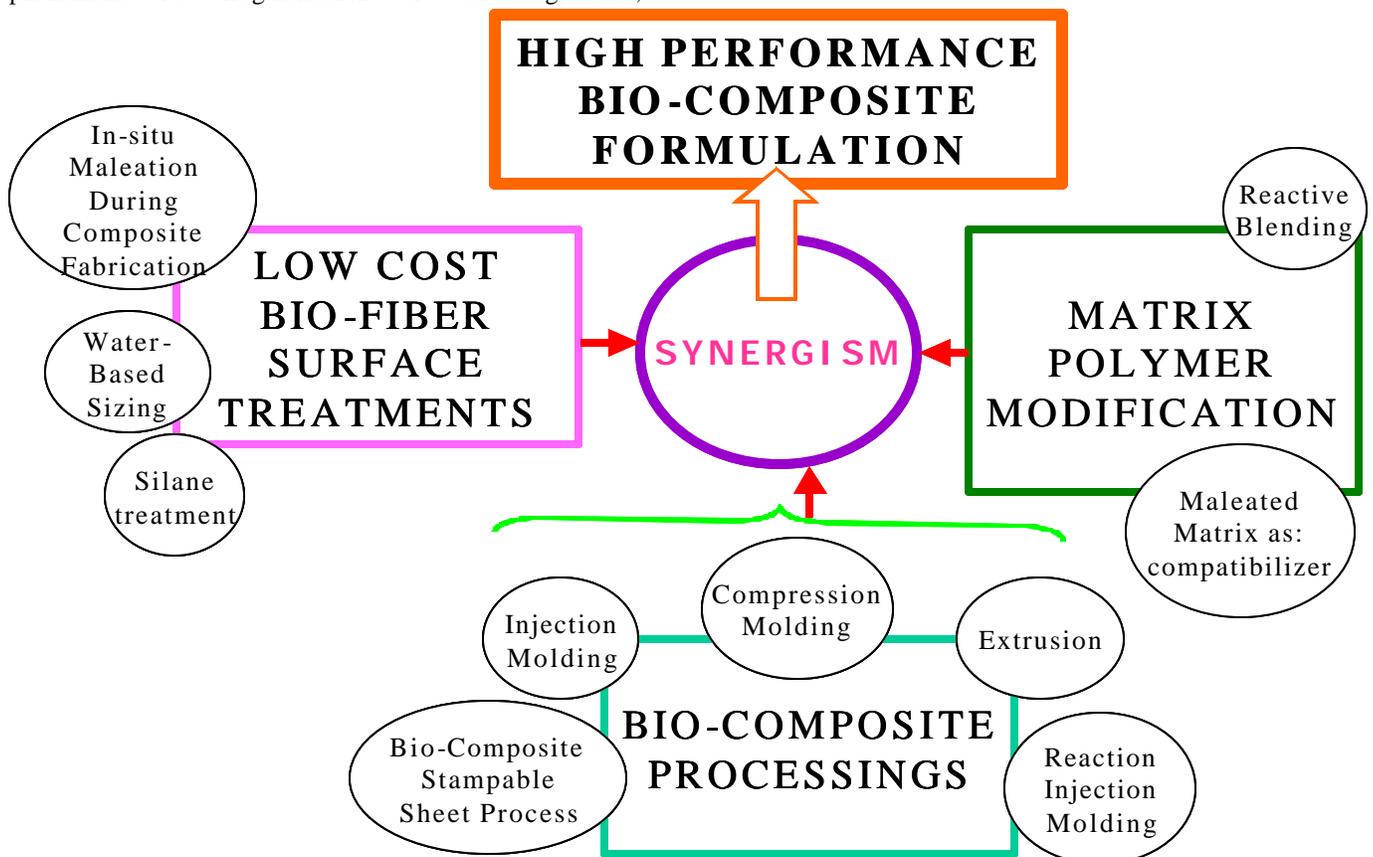
Cellulose esters are considered as potentially useful biodegradable polymers. The structures of cellulose esters including cellulose acetate (CA), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) are represented in Scheme 3. CAB and CAP now go to variety of plastic applications. For instance, premium toothbrush handle is typically made of CAP, and a screwdriver handle is often made from CAB. Recently Cellulosic plastics are gaining importance in bio-composites formulations in our group (11).

Starch is one of the least expensive biodegradable materials available in the world market today. It is a versatile biopolymer with immense potential for use in the

non-food industries. Starch based polymers can be produced from corn, wheat or potatoes. Starch is produced in plants and is a mixture of linear amylose (poly- α -1,4-D-glucopyranoside) and branch amylopectin (poly- α -1,4-D-glucopyranoside and α -1,6-D-glucopyranoside). The amount of amylose and amylopectin varies from the source. Starch can be made thermoplastic with a technology very similar to extrusion. Starch can be made thermoplastic through destructurezation in presence of specific amounts of plasticisers (water and/or poly-alcohols) in specific extrusion conditions. Three phenomena i.e. fragmentation of starch granules;

ϵ -caprolactone), PCL is compatible with many polymers and thus it is used in many formulations as compatibilizers. Recent findings showing that PCL can provide water resistance in starch-based formulations may lead to future application of large quantities of this polymer in this area.

In U.S., soybeans provide over 60% of the fats and oils used for food and majority of the feed protein. The annual production of soybeans was first recorded in 1924 at five million bushels whereas in 2000, the annual production has reached around 2.8 billion bushels. The research on applications of soybean for non-food applications in plastic and composite field is very active



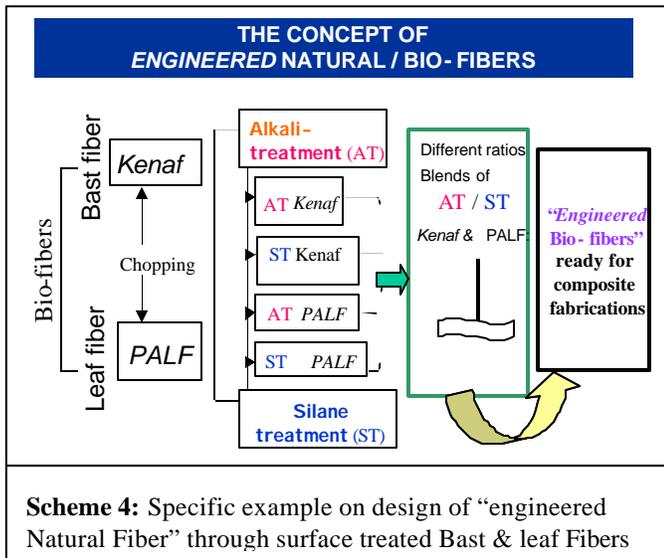
Scheme 3: Design of Superior strength bio-composites through “Synergism” of Bio-fiber surface treatment, matrix polymer modification and Composite Processing

hydrogen-bond cleavage between starch molecules leading to loss of crystallinity; and partial depolymerization of the virgin starch polymers generally occur during conversion of starch in to starch plastic through extrusion cooking. Thermoplastic starch alone can be processed as a traditional plastic; however, its sensitivity to humidity makes it unsuitable for many applications. The thermoplastic starch alone is mainly used in soluble compostable foams, such as loose-fillers, expanded trays, shape molded parts and expanded layers, as a replacement for polystyrene. Thermoplastic starch alone can be processed as a traditional plastic; however its sensitivity to humidity makes it unsuitable for many applications. Poly (

now at various U.S. Universities. Soybeans typically contain about 20% of oil and 40% of protein. Soy protein is available in three different forms as soy flour, soy isolate, and soy concentrate. Both protein and oil from soybean are converted to plastic/resin through innovative technologies. Chemically soy protein is an amino acid polymer or polypeptide while soy oil is a triglyceride. Through extrusion cooking and blending technology; soy protein polymers are converted in to biodegradable plastics whereas through fictionalization of soy oil; resin suitable in making natural fiber composites is also reported. Soy protein-based biopolymer is successfully used as polymer matrix in bio-composite fabrication (12).

Design of Superior Strength Bio-Composites

Bio-composite market is growing rapidly and so competition is expected among the industries to design superior strength bio-composites of commercial importance. The two main drawbacks of presently developed bio-composites from its rival glass fiber composites are: poor moisture resistance and low impact strength. Recent research results show that there is a large



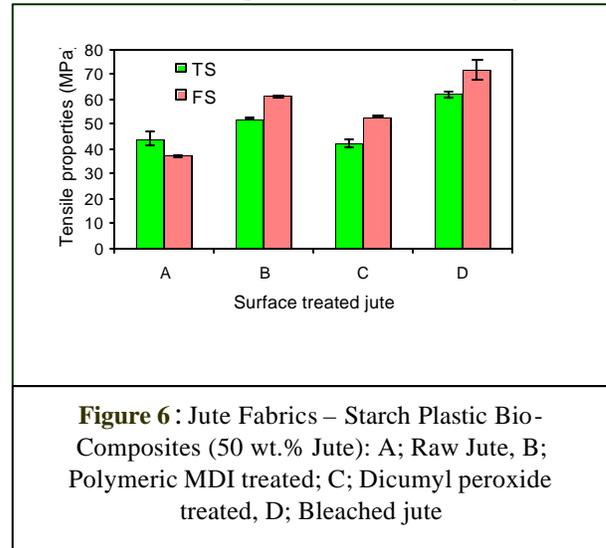
potential in improving those two properties. This potential lays either in pre-treatment of the fibers, engineering of fibers or in improving the chemistry while impregnating the fibers with the matrix polymer. Our three-corner approach in designing bio-composites of superior/desired properties include: Bio-fiber treatment; Matrix modification and Novel Processing. We target the “SYNERGISM” (Scheme 3) through above three-corner approach.

From our research results we find that bast fiber (Kenaf, Hemp etc.) based bio-composites exhibit superior flexural and tensile properties while leaf fiber (Henequen, Pineapple leaf fiber or PALF) based bio-composites show very high impact strength. Again through suitable pretreatment of bio-fibers like alkali treatment (AT) and/or silane treatment (ST) we are able to reduce the water absorption of the resulting bio-composites. Through suitable blend of such surface treated bio-fibers we design our “Engineered Natural/Bio-fibers” as shown schematically (Scheme 4).

Bio-Composite Fabrication and Performance

Eco-friendly bio-composites from plant derived fiber and crop-derived plastics would be the novel materials of the 21st century not only as a solution to the growing environmental threat but also as a solution to alleviating the uncertainty of the petroleum supply which is expected to decline between 2010 to 2020. Since Bio-

composites consist of bio-fiber and plastic from renewable resource the resulting bio-composites are expected to be biodegradable. However plastic derived from renewable resource may also be non-biodegradable depending on the structure and curing nature of such plastic during fabrication of bio-composites. For more structural and durable bio-composites; such non-biodegradable plastic resins from bio-resources offer interesting options. As for an example non-biodegradable bio-resin suitable, as a matrix resin for composite is feasible through suitable



fictionalization of vegetable oil. Thus when modifying the resin systems more or less extensively, bio-composites made from biologically renewable resources can be designed for different applications to be either biodegradable or not. Natural/Bio-fiber surface modifications, development of bio-plastic as a suitable matrix for composite fabrication and processing techniques all play vital roles in designing and engineering bio-composites of commercial interest.

In polymer matrix composites, there appears to be an optimum level of fiber-matrix adhesion to achieve best mechanical properties. The main drawback of natural fibers is their hydrophilic nature that lowers their compatibility with comparatively hydrophobic polymer matrix. The surface chemical modifications of natural fibers like dewaxing, alkali treatment, vinyl grafting, cyanoethylation, acetylation, bleaching, peroxide treatment, sizing with polymeric isocyanates, treatment with silane and other coupling agents have achieved various levels of success in improving fiber-matrix adhesion in natural fiber composites (13).

Biopolymers derived from renewable resources are just at the infancy stage and needs to be continuously developed. Starch plastics, cellulosic plastics, polylactic acid are already commercialized whereas soy –based plastics are still under developmental stage. The renewable resource-based bio-plastics like starch plastics are intended for applications like in packaging, disposables items etc. Renewable resource based bio-plastics still have niche

market over traditional plastics the reasons being the high cost and performance limitations of such bio-plastics. Through reinforcements with inexpensive bio-fibers value-added composite materials are being continuously being developed.

Natural fibers are predominantly being used in the form of chopped fiber form or in non-woven fabric forms in making bio-composites of commercial value. Woven fabrics, slivers and yarns of bio-fibers although are available but on cost/performance basis such form of bio-

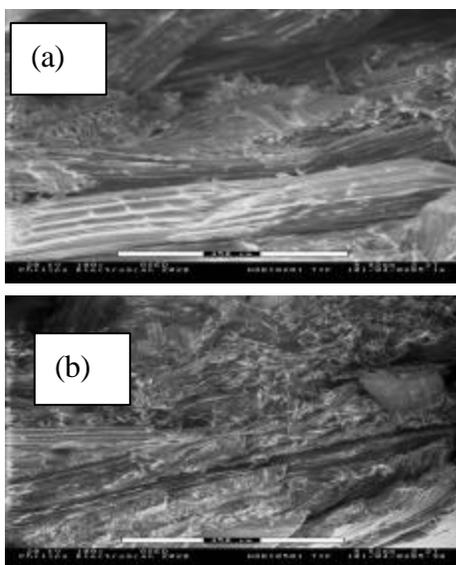


Figure 7: ESEM of (a) Raw and (b) alkali treated Hq.-Cellulose Acetate Bio-Composites (X 100): Scale 450 μ m

fibers at present are not in a state to compete with glass fiber counterparts in fiber-reinforced plastic markets. For creating composite parts, these various types of reinforcements have to be combined with matrix system in a suitable way. Since press technique meets many of the processing requirements of bio-composites, it is a frequently used manufacturing procedure. Bio-fibers in chopped form and plastic in the granule forms may be extruded uniformly in an extruder with subsequent compression molding/injection molding to get the bio-composite parts. When the thermoplastic matrix comes as a powder or solution, it is poured/mixed with the fiber uniformly, fixed by heating or drying, thus making pre-impregnated materials for the manufacture of composites by pressing. Hand-lay-up techniques, Resin Transfer Molding (RTM), Reaction Injection Molding (RIM) are the techniques used to fabricate bio-composites from bio-fibers and liquid-based resins. Thus processing techniques are to be selected mainly on the basis of fiber form, matrix type taken during bio-composite fabrications.

Through film-stacking technique we have developed bio-composites from jute fabrics and starch plastic film. The most significant result is that the tensile strength of starch plastic enhanced by more than 150% as a

result of reinforcements with bleached jute fabrics in the bio-composite containing 50 wt.% of jute (13). Influence of various surface modifications of jute on performance of jute-starch plastic composite is represented in Fig.6. Bleached jute-starch plastic composite shows tensile strength as high as 62 MPa, flexural strength of 72 MPa and high stiffness with MOE value of 4.9 GPa. Superior mechanical properties of bio-composites are based on improved fiber-matrix adhesion in case of bleached jute.

Bio-composites are developed from powder cellulose acetate bio-plastic on reinforcement with chopped henequen fiber. Henequen fiber being a hard leaf fiber, such leaf fiber based bio-composites exhibit excellent impact behavior. Unlike other biopolymers, cellulosic plastic shows better compatibility with lingo-cellulosic bio-fibers (11). The alkali treatment of henequen fiber improves the mechanical properties of the bio-composites. The alkali treatment leads to fiber fibrillation and improves surface roughness and thus creates reactive bio-fiber. Improved fiber-matrix adhesion of such alkali treated fibers is visualized from ESEM pictures of tensile fractured surfaces of bio-composites (Fig.7). Natural fiber reinforced cellulosic plastic composites show superior properties over natural fiber reinforced polypropylene composites. Through a continuous processing called as Bio-composite Stampable Sheet (BCSS) processing we are targeting to manufacture high volume bio-composites for industrial applications especially in designing eco-friendly green bio-composites for automotive applications. Through film-stacking techniques as well as extrusion processing we are designing sustainable bio-composites from natural fiber and PLA polymers. The “engineered bio-fiber” concept is successfully implemented in manipulating the flexural and impact properties of the resulting PLA-based bio-composites (12). Through reactive blending of soy protein, plasticizer and low content of commercial bio-polymer; we are developing new soy-based bio-plastic. The soy-based bio-plastic on reinforcements with bio-fibers result in eco-friendly bio-composites. Injection molded soy-based composites show superior mechanical properties over compression molded counterparts (12) as found from our recent investigations.

New process development for bio-composite fabrications for commercial applications is the real challenge of research at the current level of technology so far developed for bio-composites.

Most work on natural fiber – thermoplastic composites is based on melt mixing in a kinetic mixer followed by injection/compression molding. Such processing conditions reduce the desirable physical and mechanical properties because of damage of the natural fiber due to high shear. The excellent physical and mechanical properties of bio-fibers would be available only when processing methods reduce or eliminate fiber damage to the greatest possible extent. An alternative processing method is the application of powder impregnation technology. Dry powder processing is a

technology that is : i) environmentally benign, since no organic solvent is used thus a VOC (Volatile organic content)-free technology, ii) low cost, iii) free from exposure of high shears for natural fibers.

One of our novel approaches in making Bio-Composites is through a process, which calls as Bio-Composite Stampable Sheet Process (BCSS). Powder impregnation technology and electrical alignment of bio-fibers are targeted in designing superior strength bio-composites. BCSS process consists of:

- The intermingling of various combinations of chopped natural fibers (raw as well surface modified) with powder polymer;
- Application of an electrical field to align the natural fibers;
- Partial consolidation via sintering the polymer powder to bridge and hold the fibers in place; and
- Finally producing the biofiber-polymer composite in either thin or thick sheets suitable for subsequent forming and consolidation with low-pressure molding.

Conclusions

After decades of high-tech developments of artificial fibers like aramid, carbon and glass it is remarkable that natural fibers have gained a renewed interest, especially as a glass fiber substitute in automotive industries. New environmental regulations and societal concern have triggered the search for new products and processes that are compatible to the environment. The incorporation of bio-resources in to composite materials can reduce further dependency of petroleum reserves. The major limitations of present biopolymers are their high cost. Again renewable resource based bio-plastics are currently being developed and need to be researched more to overcome the performance limitations. Bio-composites can supplement and eventually replace petroleum based composite materials in several applications thus offering new agricultural, environmental, manufacturing and consumer benefits. The main advantage of using renewable materials is that the global CO₂ balance is kept at a stable level. Several critical issues related to bio-fiber surface treatment to make it more reactive, bio-plastic modification to make it a suitable matrix for composite application, and processing techniques depending on the type of fiber form (chopped, non-woven/woven fabrics, yarn, sliver etc.) need to be solved to design bio-composites of commercial interests. Bio-composites are now emerging as a realistic alternative to glass reinforced composites. Bio-composites being derived from renewable resources; the cost of the materials can be markedly reduced with their large-scale usage. Recent advances in genetic engineering, natural fiber development and composite science offer significant opportunities for improved value-added materials from renewable resources with enhanced support of global sustainability. Thus the main motivation for developing

bio-composites has been and still is to create a new generation of fiber reinforced plastics with glass fiber reinforced – like or even superior properties that are environmentally compatible in terms of production, usage and removal. Natural fibers are biodegradable but renewable resource-based bio-plastic can be designed to be either biodegradable or not according to the specific demands of a given application. The raw materials being taken from renewable resources, bio-composites are prone to integrate in to natural cycle. The general environmental awareness and new rules and regulations will contribute to an increase in the work for more Eco-friendly concept in the automotive industry.

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